chemical kinetics and equilibrium

The degree to which a chemical reaction proceeds to form a useful product and the time required to complete the conversion are two important aspects of modern chemistry. Chemical kinetics is the study of factors important to the speed at which a reaction forms product molecules. The final distribution of products and unconsumed reactants is often predetermined by the nature of the process and is representative of the chemical equilibrium, or balance, that is achieved.

CHEMICAL KINETICS

Chemical kinetics is the study of the rates of chemical reactions and the factors that control both the yields of product molecules and the consumption of the reacting species. A detailed molecular picture showing the process at the most elementary level is known as a reaction mechanism.

Reaction Rates

A measure of the speed at which a reaction proceeds to form products is given by the reaction rate law, a relation based on experimental measurements. If molecules A and B react to form products C and D, this process may be written as:

A + B form C + D

The rate of the reaction expresses the speed at which A or B is lost, or C or D is created, and might be determined as:

Rate = k[A][B]

where k is proportionality constant (the rate constant) and the brackets around A and B indicate that their concentrations are to be used in the rate equation. Such a simple rate law is appropriate if the reaction is the result of a collision in which one molecule of A strikes one molecule of B to form the chemical products. This collision would be an example of an elementary process (in this case a bimolecular reaction), and the association with the simple rate is straightforward. The molecularity of the reaction is the number of reactant molecules that participate in the elementary process (in this case, two).

Many reactions involving only two chemical components are more complex and involve unstable species known as chemical intermediates that do not appear in the reaction equation. In such cases the rate expression is more complicated and must be determined by experimental variation of the concentrations of the reaction components.

Reactions at surfaces are extremely important in the chemical industry and often proceed at high efficiencies. If a solid is dispersed in a reaction mixture, the surface area of the particles limits the exposure of the material and the rate of the reaction. Large surface areas of finely ground powders generally lead to increased reactivity.

Another common reaction is the unimolecular process, in which a single chemical component decomposes into products. The kinetic expression for this is: Rate = k [Reactant]. The molecularity of the reaction is one. Many simple reactions induced by high temperatures or exposure to ultraviolet radiation proceed in this manner.

The order of a reaction is the simple sum of the exponents of the concentration terms in the rate expression. For the unimolecular process the order of the reaction is one. For the bimolecular reaction, the order is two, since both [A] and [B] are raised to the first power. In more complex processes, fractional exponents and negative exponents are possible in the rate law, and the order of the reaction reflects the presence of intermediates or the hidden complexity of the reaction.

Because collisions between molecules often control the formation of products or chemical intermediates, a simple model for treating the dynamics of reactions is available, based on the KINETIC THEORY OF MATTER. The effect on the observed reaction rate of increasing the concentrations of the reactants can be viewed in terms of the increased number of collisions. The effect of temperature on the reaction rate, often a complex matter, is related to the higher velocities and energies available to the reactants as the temperature of the reaction mixture is increased. Merely bringing the molecules together is not sufficient if an added amount of energy is necessary to promote the formation of the products. This energy is the activation energy of the reaction. A high activation energy generally inhibits the reaction and results in a slow reaction rate. Raising the temperature and thus the

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energies of the reactants is one method for accelerating the rate of the reaction.

Catalysts

A catalyst is a material that is added to a reaction mixture to accelerate the process but is itself not consumed. Rates may be increased by several orders of magnitude by trace amounts of these substances. On a microscopic scale the catalyst's role may be complex, but it has the end result of many cases reactions that would normally require high temperatures can be run at room temperature, with substantial savings in the cost of electricity or heating fuel. In biological systems many slow processes are enhanced through the use of highly selective biochemical catalysts called enzymes.

CHEMICAL EQUILIBRIUM

In the previous discussion of reaction rates, the general processes noted resulted in the formation of products, with the reactions proceeding from left to right as written. Many processes are reversible. If a mixture of A and B, C and D, or of three or all four of the components is placed in a reaction chamber at fixed temperature, the reactions will proceed and eventually reach a special state. At this point the rates of the forward and of the reverse reaction are equal. This final state is reached regardless of the original composition of the mixture, and is approached in a spon taneous manner. At this point chemical equilibrium has been achieved, and subsequent probing of the mixture will show that no net change in the concentrations of the chemical components is occurring.

Nothing is said of the rates of the reactions or of the time needed for the system to reach this equilibrium. Indeed, without the use of a catalyst or extremely high temperatures to accelerate the reaction, the time needed to reach this equilibrium state is on the order of centuries.

Le Chatelier's Principle

Once a chemical system has reached equilibrium, effects due to changes in the temperature or pressure, or due to the addition or removal of chemical species, can be predicted using simple relations described by Henri Le Chatelier in 1884. A system that is stressed will adjust its character to relieve the stress. If the external pressure is increased, the reaction can effectively occupy a smaller volume by moving toward product, since two molar volumes of product are generated from four molar volumes of reactants. The reaction is known to release energy in forming products. The effect of increasing the temperature is therefore relieved by generating reactants that consume the added energy. Recall, however, that the equilibrium constant usually refers to a fixed temperature, and that its value can change radically as a function of temperature.

Energetics and Chemical Equilibrium

The character of the equilibrium state reflects the delicate balance between two fundamental concepts of thermodynamics: ENTHALPY and ENTROPY. Enthalpy, the measure of the energy stored in the chemical bonds of molecules, facilitates a comparison of the relative stabilities of the reactants and products. Bond formation and stabilization of energy are preferred in the competition between reactants and products. Entropy is a measure of the freedom or randomness that is favored in physical properties of matter.

Equilibrium Expressions

Although the previous discussion of equilibrium systems centered on simple reactions between gases or molecules in solution, many other situations arise. Many ionic solids, such as salt, NaCl, readily dissolve in solution, and ionic equilibrium expressions are applicable. Sodium cations and chlorine anions are in dynamic equilibrium with the solid NaCl. In many industrial processes a reaction is facilitated by the addition of a solid catalyst that does not go into solution (a heterogeneous catalyst), and a suitable equilibrium expression can be applied. Many OXIDATION AND REDUCTION reactions are important in the fields of electrochemistry and metallurgy. In these processes electrons are exchanged between reactants or products, and equilibrium expressions are employed to predict the direction and efficiency of the reactions. An electric battery is a self-contained chemical system in which the energy exchanged in a spontaneous electron transfer is employed to generate a small voltage. Equilibrium expressions can be used to determine the amounts of reactants and products involved in this common chemical process.

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